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Versatile Reaction Patterns of Phosphanylhydrosilylalkyne with $B(C_6F_5)_3$: Remarkable Group Substitution Effect

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Supplementary Information (ESI) available: Table for crystal data and refinements, kinetic study, DFT calculation details, collected NMR spectra. CCDC: CCDC 2004665 (**2**), 1903424 (**4**), 1903425 (**5**), 1903427 (**7**), 1903429 (**8**), 1903430 (**9**), 1903431 (**10**), and 1903433 (**11**).

Abstract: Phosphanylhydrosilylalkynes $R_2HSiCCPAr_2$ (R,Ar: Me,4-*t*BuC_6H_4 **1**, Me,Mes **2**, Mes,Ph **3**; Mes = 2,4,6-$Me_3C_6H_2$) were prepared and the reactions with $B(C_6F_5)_3$ were studied. Reaction of **1** and $B(C_6F_5)_3$ produced *E*-alkene {(*E*)-$(C_6F_5)_3$BCHC[P(4-*t*Bu$C_6H_4)_2$]SiMe_2}$_2$ (**4**) and that of **2** and $B(C_6F_5)_3$ yielded *Z*-alkene (*Z*)-$(C_6F_5)_2$BCHC(PMes_2)Si$Me_2(C_6F_5)$ (**5**). The former is proposed to go through a key $[Me_2HSi]^+$ for function while the latter via the phosphacyclopropene intermediate, both of which are a result by self-hydrosilylation. Reaction of **3** and $B(C_6F_5)_3$ generated at room temperature a P→B coordination compound $Mes_2HSiCCP(Ph_2)B(C_6F_5)_3$ (**6**) and at 100 °C the 1,1-carboboration *E*-alkene (*E*)-$Mes_2HSi(Ph_2P)CC(C_6F_5)B(C_6F_5)_2$ (**7**). Kinetic study and DFT calculations were accomplished for reaction of **2** and $B(C_6F_5)_3$ to **5**. The mechanisms of these reactions have been discussed. The reactions of the P/Si^+ LPs $Me_2Si(Ph_2P)CCHB(C_6F_5)_3\}_2$ (**3a**) and **4** were also investigated. Compound **4** disassociated H_2O into {(*E*)-$(C_6F_5)_3$BCHC[PH-4-*t*Bu$C_6H_4)_2$]Si$(Me_2)\}_2(\mu$-O) (**8**) and (*E*)-$(C_6F_5)_3$BCHC[PH(4-*t*Bu-$C_6H_4)_2$]Si(Me_2)O(HNC_5H_5) (**9**). Compound **3a** reacted with *t*BuNCO by [3+2] dipolar cycloaddition to give a C_2OPSi-heterocycle [$(C_6F_5)_3$BHC]CSi(Me_2)P(Ph_2)OC(N*t*Bu) (**10**). Furthermore, **4** reacted with *t*BuNCO and then H_2O to afford (*E*)-$(F_5C_6)_3$BHCC[P(4-*t*Bu$C_6H_4)_2$C(O)NH*t*Bu][Si(Me_2)O$H(NC_5H_5)$] (**11**) through a C_2OPSi-heterocycle intermediate followed by the H_2O-disassociation under the C_2OPSi-ring opening.

Introduction

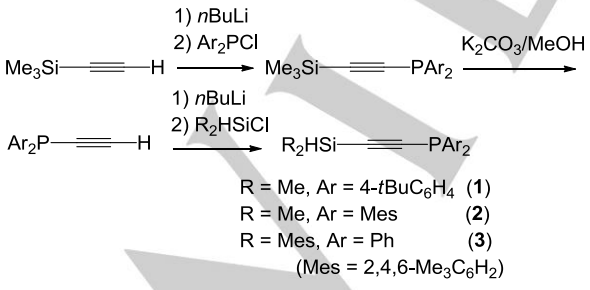
Hydrosilylation has now become a convenient and important way for production of functionalized silanes.[1] Progress of such reaction, however, meets often with difficulty due to relatively inert reactivity of the SiH functionality contained in hydrosilanes as the reagent species.[1] Promotion of the SiH reactivity for function is thus of great research effort and the number of routes has been reported. The hydrosilylation of 1-octene into *n*-octyltrichlorosilane was early reported, which was thought to be promoted by the peroxide radical when trichlorosilane was used.[2] Efficiency of the hydrosilylation was later found upon catalysis by the transition metal (M), where the SiH group was able to convert into the MH and/or M-silyl that is (or are) highly active facilitating reactions toward alkene,[3] alkyne,[4] and ketone and aldehyde,[5] although the related mechanisms were proposed to be diverse. In recent years, the borane-promoted hydrosilylation of unsaturated organics has attracted particular attention because of advantage either as a mild method or without use of the transition metal. Notably, Piers and co-workers have cleanly demonstrated a Si−H···$B(C_6F_5)_3$ activation mode that conducts well hydrosilylation of the C=O or C=N bond molecules in catalysis, by means of which an interaction of the O or N donor at the Si nucleus allows the bond rearrangement into the $[HB(C_6F_5)_3]^-$ for further H^- transfer to the multiple bond C atom finalizing the catalytic cycle.[6] Then Oestreich and co-workers showed a combination of cyclohexa-2,5-dien-1-ylsilanes as the surrogate, where $B(C_6F_5)_3$ was able to form $[HB(C_6F_5)_3]^-$ and $[R_3Si(C_6H_6)]^+$ for addition into the C≡C bond of PhCCPh.[7] Ingleson and Curless reported on the $B(C_6F_5)_3$-catalyzed hydrosilylation of 4-RC_6H_4CCR' by Ph_2SiH_2 through forming the Ph_2HSi–$(\mu$-H)–$B(C_6F_5)_3$ intermediate in work.[8] These results together with other related studies[9] showed that activation of the Si−H bond for function appears more favourable than that of the C=O, C=N, or probably C≡C bond of substrates.[10]

Aluminium hydrides (R'$_2$HAl, R'$_2$ is dianionic group(s)) are commonly known to carry well the hydroalumination of multiple bond organics without promotion because of the strong Lewis acidity of the Al center.[11] To be compared, the silylium ion of the type of $[R_2HSi]^+$ (R_2 is dianionic group(s)) is isoelectronic and isolobal to the R'$_2$HAl in essence. Such species are reported rarely and only several compounds $[PhH_2Si]^+[(C_6F_5)_2HB$-$CH_2CH_2PMes_2]^-$,[12] $[Ph_2HSi]^+[(C_6F_5)_2HBCH_2CH_2PMes_2]^-$,[12] $[(C_5Me_5)_2HSi]^+$-$[C_6H_4O_2H_3O_2C_6H_4]^-$,[13] and $[t$Bu$_{3-n}$H$_n$Si$]^+[CHB_{11}H_5Br_6]^-$ (n = 1 and 2)[14] were found and well characterized. An open question is then arising whether such $[R_2HSi]^+$ is capable of the hydrosilylation. Up to now no such reaction was documented. We have recently prepared the phosphanylhydrosilylalkyne, a functionalized alkyne of the

new type containing the PAr_2 and $SiHR_2$ substituents.[15] However, no reaction was direct to the adjacent SiH group and C≡C bond even upon heat treatment. Nonetheless, it was found that such alkyne readily reacted with $B(C_6F_5)_3$ to form two types of the alkenes as the respective P/Si^+ and P/B Lewis pairs (LPs) both as a result by self-hydrosilylation. Combined reaction kinetics and DFT calculations disclosed the $B(C_6F_5)_3$-promoted formation of the $[R_2HSi]^+$ *in situ* for function.[15] This indicates, to our knowledge, a new way to improve the SiH reactivity for work. Of particular importance, this reaction results in unique way to produce the P/Si^+ and P/B LPs, of which the former P/Si^+ LP is rare and the way to it is significantly distinguished from the routes by reacting the as-made FLP with terminal alkyne,[16] the silane with $R_3P/[Ph_3C]^+[B(C_6F_5)_4]^-$,[17] or Me_3SiOTf with *p*-block Lewis bases.[18] We herein report that changes of either the hydrosilyl or phosphanyl groups, as expansion of such functionalized alkyne, have a great influence on the reaction pattern of the phosphanylhydrosilylalkynes newly prepared when treated with $B(C_6F_5)_3$. The reactions of the derived P/Si^+ LPs with water and/or isocyanate were also investigated.

Results and Discussion

Starting from Me_3SiCCH, phosphanylhydrosilylalkyne $R_2HSiCCPAr_2$ was prepared through a C≡C-centered, three-folded substituent transformation (Scheme 1). An *n*BuLi deprotonation followed by LiCl-elimination with Ar_2PCl led smoothly to $Me_3SiCCPAr_2$ that underwent a Me_3Si/H exchange in the presence of MeOH and K_2CO_3 to give $HCCPAr_2$. Compound $HCCPAr_2$ reacted again by the *n*BuLi deprotonation and then the LiCl-elimination using R_2HSiCl to result in the target compound. This way has been demonstrated to be straightforward and effective for synthesis of compounds $Me_2HSiCCPPh_2$ (**1a**) and $Me_2HSiCCP(4\text{-}MeC_6H_4)_2$ (**2a**).[15] By changing the PAr_2 group, compounds $Me_2HSiCCP(4\text{-}tBuC_6H_4)_2$ (**1**, an off-white solid, 85% yield) and $Me_2HSiCCPMes_2$ (Mes = 2,4,6-$Me_3C_6H_2$, **2**, an orange solid, 71% yield) were synthesized. While alternating the R_2HSi group, compound $Mes_2HSiCCPPh_2$ (**3**, a slight-grey solid, 75% yield) was produced.



Scheme 1. The C≡C-centered, three-folded substituent reaction to form phosphanylhydrosilylalkynes **1**–**3**.

Compounds **1**–**3** are characterized by NMR and IR spectroscopy as well as by elemental analysis. Table 1 summarizes characteristic NMR data for groups of *SiH*R_2, *C*≡*C* and *P*Ar_2 in **1**–**3** together with those in **1a** and **2a** for comparison. Compound **1** holds the $SiHMe_2$ and $P(4\text{-}tBuC_6H_4)_2$ substituents and the ^1H, ^{29}Si and ^{31}P NMR spectra record the resonances at δ_{Si} –37.6, δ_H 4.24, and δ_P –35.6 ppm respectively, close to those found in **1a** and **2a**. Compound **2** contains the $SiHMe_2$ and $PMes_2$, and then the silicon (δ_{Si} –38.1 ppm) and proton (δ_H 4.12 ppm) resonances are comparable, but the phosphorus resonance (δ_P –54.7 ppm) appears at a higher field. In comparison, compound **3** has the $SiHMes_2$ and PPh_2 and exhibits the phosphorus resonance (δ_P –31.5 ppm) near to those in **1a**–**2a** and **1**, but the silicon (δ_{Si} –61.1 ppm) and proton (δ_H 5.62 ppm) resonances markedly shifted. Clearly, ligation of the Mes group gives rise to a particular effect on the electronic environment and then the NMR resonance around either the P or Si nucleus when compared with that of the other groups. Nonetheless, the alkynyl carbon resonances ($\delta_{PC\equiv}$ 105.2–107.2 and $\delta_{SiC\equiv}$ 112.7–113.5 ppm) in **1a**–**2a** and **1**–**3** are close, irrespective of the change of the $SiHR_2$ and PAr_2 substituents. The IR spectrometry exhibits the Si–H (at ν 2141 cm^{-1} in **1**, 2126 cm^{-1} in **2**, and 2148 cm^{-1} in **3**) and C≡C (at ν 2104 cm^{-1} in **1**, 2086 cm^{-1} in **2**, and 2091 cm^{-1} in **3**) bond vibrations in character respectively, which are comparable to those found in **1a** and **2a**.[15] Compound **2** is further characterized by X-ray crystallography, which confirms composition and structure in line with those analyzed by the aforesaid NMR and IR spectroscopy. Of notice is exhibition of a pyramidal geometry at the P atom in **2**, as indicates existence of a lone electron pair around the P center (Figure 1).

Table 1. Summarized NMR data for groups of **1a**−**1b** and **1**–**3**.

Comp.	^1H NMR	^{13}C NMR		^{29}Si NMR	^{31}P NMR
	Si*H*	Si*C*≡	≡*C*P		
1a	4.45	113.5	105.2	−37.4	−32.5
2a	4.26	112.7	106.0	−37.5	−34.4
1	4.24	112.7	106.0	−37.6	−35.6
2	4.12	112.8	106.8	−38.1	−54.7
3	5.62	113.2	107.2	−61.1	−31.5

1a $Me_2HSiCCPPh_2$ and **2a** $Me_2HSiCCP(4\text{-}MeC_6H_4)_2$.

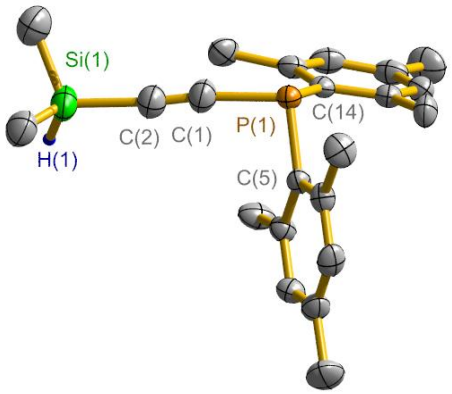
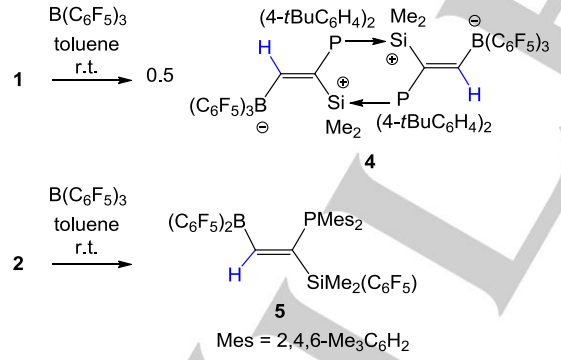
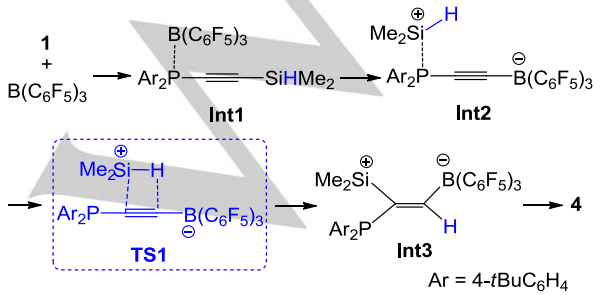


Figure 1. X-ray crystal structure of **2** with thermal ellipsoids at 50% probability level. H atoms except for those of SiH are omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.198(4), C(1)–P(1) 1.771(3), C(2)–Si(1) 1.886(5) (av), Si(1)–H(1) 1.46(5) (av); P(1)–C(1)–C(2) 167.2(3), C(1)–C(2)–Si(1) 164.0(3), C(1)–P(1)–C(5) 109.47(11), C(1)–P(1)–C(14) 98.75(10), C(5)–P(1)–C(14) 104.21(10).

Reaction of **1** with equivalent $B(C_6F_5)_3$ was monitored by the ^1H and ^{31}P NMR spectra in $CDCl_3$ from –70 to 25 °C, which revealed a process similar to that of **1a** and $B(C_6F_5)_3$ to generate $[(E)$-$(C_6F_5)_3BCHC(PPh_2)SiMe_2]_2$ (**3a**) and (Z)-$(C_6F_5)_2BCHC(PPh_2)SiMe_2(C_6F_5)$ (**5a**) or of **2a** and $B(C_6F_5)_3$ to $\{(E)$-$(C_6F_5)_3BCHC[P(4\text{-}MeC_6H_4)_2]SiMe_2\}_2$ (**4a**) and (Z)-$(C_6F_5)_2BCHC[P(4\text{-}Me\text{-}C_6H_4)_2]SiMe_2(C_6F_5)$ (**6a**).[15] This suggests a probable common pattern conducted for these reactions,[15] essentially due to close electronic property of the phosphanylhydrosilylalkyne with respect to the PAr_2 (Ar = Ph (**1a**), 4-MeC_6H_4 (**2a**), 4-*t*BuC_6H_4 (**1**)) *versus* the $SiHMe_2$ substituent as indicated by the NMR data. The large-scale reaction in toluene at room temperature afforded compound $\{(E)$-$(C_6F_5)_3BCHC[P(4\text{-}tBuC_6H_4)_2]SiMe_2\}_2$ (**4**, Scheme 2) that was precipitated as an off-white solid in a yield of 35%. A suggested formation of **4** is enhanced in Scheme 3. However, an attempt to isolate another compound was not successful due to formation of a messy mixture after separation of **4**. Compound **4** is characterized by NMR spectroscopy and X-ray crystallography, which features a dimer structure (Figure 2), comparable to that of **3a** or **4a**.[15] The P(1)–Si(1) bond length is 2.3241(6) Å and compares well with those in **3a** (2.323(1) Å) and **4a** (2.314(1) Å). In other related species of $(C_6F_5)_2HBCH_2CH_2(Mes)_2P\rightarrow SiH_2Ph$ (2.309(1) Å),[12] $[Me_3Si\leftarrow P(Me_2)CH_2CH_2(Me_2)P\rightarrow SiMe_3]$-$(OSOCF_3)_2$ (2.3061(1) Å),[18] $(Me_3P\rightarrow SiMe_3)(OSOCF_3)$ (2.294(1) Å),[18] $(tBu_3P\rightarrow Si\text{i}Pr_3)[B(C_6F_5)_4]$ (2.4843(5) Å),[17] and $(tBu_3P\rightarrow SiPhMe_2)[BH(C_6F_5)_3]$ (2.3764(8) Å),[19] varied P–Si lengths are found because of the group steric influence. In the structure of monomeric part, newly formed C=C bond (1.359(3) Å) is surrounded by four substituents H, $B(C_6F_5)_3$, $P(4\text{-}tBuC_6H_4)_2$, and $SiMe_2$ in an *E*-configuration. The B, Si, and P centers all are four-coordinate, adopting the tetrahedral geometry. The B atom holds the negative charge whereas the Si center the positive charge. Compound **4** is an alkenyl-linked silylium borate.



Scheme 2. Reactions of **1** and **2** each with $B(C_6F_5)_3$ to form **4** and **5**.



Scheme 3. Postulated reaction mechanism for **1** and $B(C_6F_5)_3$ to **4**.

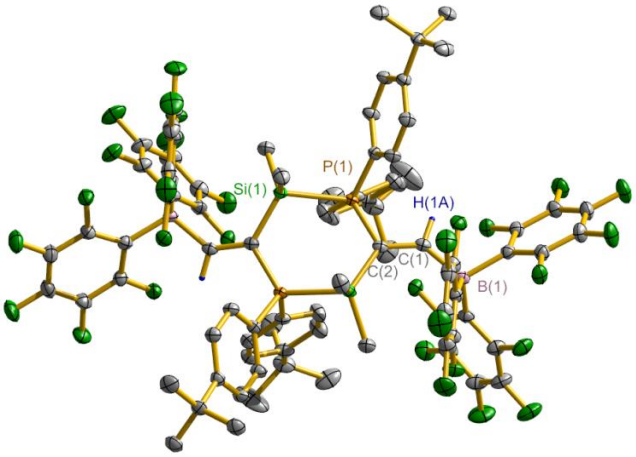


Figure 2. X-ray crystal structure of **4** with thermal ellipsoids at 50% probability level. H atoms except for those of =CH are omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.359(3), C(1)–B(1) 1.649(3), C(2)–Si(1A) 1.8717(18), C(2)–P(1) 1.8156(18), P(1)–Si(1) 2.3241(6); C(1)–C(2)–Si(1) 127.50(14), C(1)–C(2)–P(1) 114.25(13), C(2)–C(1)–B(1) 133.57(16), C(2)–C(1)–H(1A) 113.2, P(1)–C(2)–Si(1) 118.22(10).

Under similar condition, compound **2** reacted with $B(C_6F_5)_3$ to give product (Z)-$(C_6F_5)_2BCHC(PMes_2)SiMe_2(C_6F_5)$ (**5**, Scheme 2) that was isolated as colorless crystals in 55% yield. It was noted that this reaction proceeded through apparent color changes from orange to red, dark red, and then this dark red faded gradually. This process is in sharp contrast to that of the former reaction by keeping little color change in the course, implying undergoing of a probably differed reaction mode. Compound **5** is characterized by NMR spectroscopy and X-ray crystallography, which displays a structure differing from **4** (**3a** or **5a**) indeed but resembling to **4a** or **6a**.[15] A phosphaboracyclobutene of **5** is formed owing to a strong P–B bonding (2.118(3) Å, Figure 3), and around the C=C bond (1.341(4) Å) are four groups H, $B(C_6F_5)_2$, $PMes_2$, and $SiMe_2(C_6F_5)$ arranged in a *Z*-configuration. The P(1)–C(2)–C(1) (96.0(2)°) and B(1)–C(1)–C(2) (110.0(3)°) bond angles significantly deviate from the alkenyl 120° indicative of a C_2BP-ring strain character. We performed further the ^1H and ^{31}P NMR spectra-monitored reaction of **2** with $B(C_6F_5)_3$ in $CDCl_3$ from –70 to 25 °C. As shown in Figure 4, an *H*Si resonance at δ_{SiH} 4.12 ppm assigned to **2** was gradually consummed and the *H*C= one at $\delta_{HC=}$ 8.68 ppm to **5** formed instead. This discloses a general reaction conversion process. During this course were found mediation of several other resonances. The resonance at δ_{SiH} 4.75 ppm might correspond to $Me_2HSiCCP(Mes_2)\rightarrow B(C_6F_5)_3$ (**Int1′**), as comparable data are detected for similar $Mes_2HSiCCP(Ph_2)\rightarrow B(C_6F_5)_3$ (δ_{SiH} 5.59 ppm, *vide infra*) and $Me_2HSiCCP(Ph_2)\rightarrow B(C_6F_5)_3$ (δ_{SiH} 4.70 ppm).[15] The resonance at δ_{SiH} 4.10 ppm as a doublet could be from a phosphacyclopropene $Mes_2PC_2[B(C_6F_5)_3](SiHMe_2)$ (**Int2′**) since its $PMes_2$ resonance was observed at δ_{PMes2} −151.2 ppm (Figure S1 in the SI) which is close to those in $Mes_2PC_2[B(C_6F_5)_3]Ar$ (Ar = 4-MeC_6H_4, δ_{PMes2} −137.8 ppm; Ar = Ph, δ_{PMes2} −137.4 ppm) reported by Erker and coworkers.[20] Accordingly, we reason that the reaction of **2** and $B(C_6F_5)_3$ to **5** occured by a starting P→B coordination interaction to form **Int1′** that proceeded further *via* a

$(C_6F_5)_3B$-$PMes_2$ exchange resulting in **Int2'**. The **Int2'** reacted by an H-group 1,3-transfer under the PC_2-ring opening to give **Int3'** ($\delta_{HC=}$ 9.10 and $\delta_{PMes2=}$ 23.8 ppm) that was followed by a C_6F_5-migration (Scheme 4). It was mentioned that occurance of the complicated color changes during the reaction might be due to formation of the PC_2-ring **Int2′**. We have tried isolation of this species by controlling the reaction at low temperature, but were not successful. The particular formation of the **Int2′** ought to be induced due to unique electronic property of the $PMes_2$ substituented at the C≡C bond.

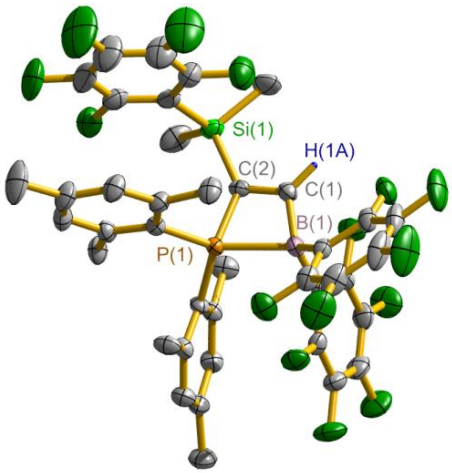


Figure 3. X-ray crystal structure of **5** with thermal ellipsoids at 30% probability level. H atoms except for that of =CH are omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.341(4), C(1)–B(1) 1.603(5), C(2)–Si(1) 1.867(3), C(2)–P(1) 1.817(3), P(1)–B(1) 2.118(3); Si(1)–C(2)–C(1) 124.1(2), P(1)–C(2)–C(1) 96.0(2), B(1)–C(1)–C(2) 110.0(3), H(1A)–C(1)–C(2) 125, P(1)–C(2)–Si(1) 137.34(18), C(2)–P(1)–B(1) 75.35(14), C(1)–B(1)–P(1) 77.69(17).

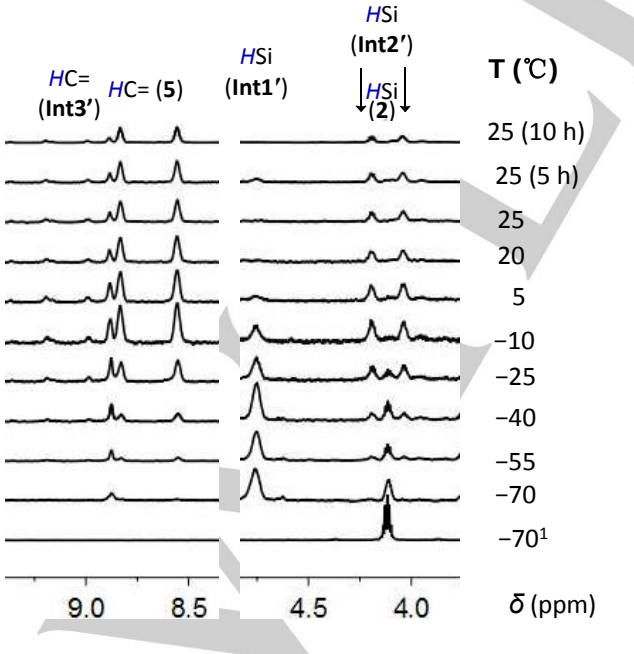
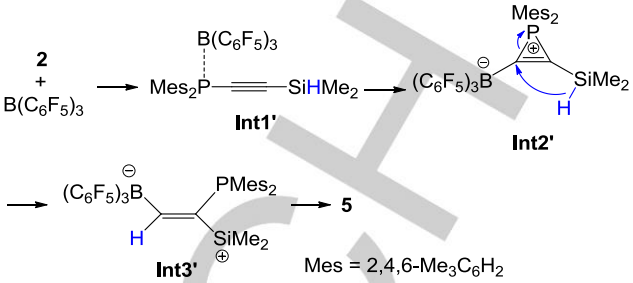


Figure 4. [1]H NMR spectra-recorded variable-temperature (from –70 to 25 ºC) reaction of **2** and $B(C_6F_5)_3$ in $CDCl_3$ on Bruker Avance II 400. The resonances at δ 3.75−4.85 ppm are due to the Si*H*Me_2 and at δ 8.25−9.25 ppm to the *H*C=. [1] Data for **2** at –70 ºC before addition of $B(C_6F_5)_3$.



Scheme 4. Postulated reaction mechanism for **2** and $B(C_6F_5)_3$ to **5**.

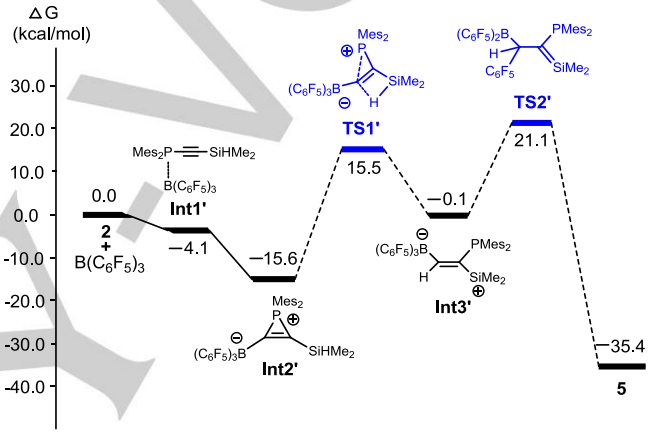
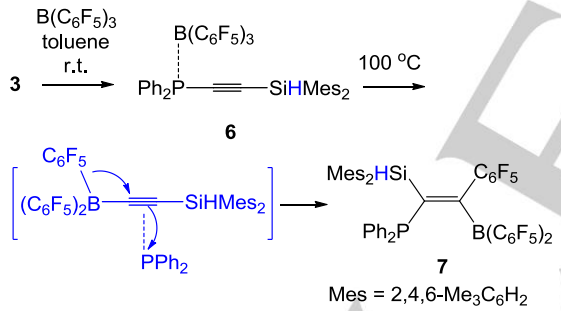


Figure 5. Computed free energy profile (kcal/mol) for reaction of **2** and $B(C_6F_5)_3$ to **5** at the M06-2X/def2-SVP level.

We furthermore accomplished DFT calculations at the M06-2X/def2-SVP level to detect this complicated process. The study details that the P→B coordination between **2** and $B(C_6F_5)_3$ is thermodynamically favoured by ΔG of –4.1 kcal/mol leading to **Int1'**. Subsequent $(C_6F_5)_3$B-$PMes_2$ exchange forming **Int2'** is also smoothly going with further exothermic energy of 11.5 kcal/mol. This process compares significantly different from the $(C_6F_5)_3$B-$SiHMe_2$ group exchange to generate the **Int2**-type species (Scheme 3), where a chemical change of the $Me_2HSiCCP(Ph_2)$→$B(C_6F_5)_3$ into the $(C_6F_5)_3BCCP(Ph_2)$→$SiHMe_2$ was calculated to absorb an energy by 13.0 kcal/mol for compensation in the reaction of **1a** and $B(C_6F_5)_3$ to **3a** and **5a** we previously reported.[15] The conversion to **Int3′** requires to overcome a **TS1′** barrier (at 15.5 kcal/mol), and then an intermolecular C_6F_5-migration to form **5** still goes through a **TS2′** barrier (at 21.2 kcal/mol) under an energy releasing of 56.5 kcal/mol (Figure 5). It is deserved to mention that there suggests another possible **TS1a′** state (Scheme S1 in the SI). Due to a higher energy level (at 25.3 kcal/mol), the **TS1a′** was thought not to involve although it converts into **5′** through the **Int3a′** without any barrier. As a result, the reaction of **2** and $B(C_6F_5)_3$ yielded only compound **5**, as is in agreement with the experiment.

The reaction using **3** with equivalent $B(C_6F_5)_3$ was carried out in toluene at room temperature as usual, which, however, led to

a prompt formation of compound $Mes_2HSiCCP(Ph_2)B(C_6F_5)_3$ (**6**) that was isolated as a colorless oil in an almost quantitative yield. Upon heat treatment at 100 °C for 48 h such reaction further produced another compound (*E*)-$Mes_2HSi(Ph_2P)CC(C_6F_5)B(C_6F_5)_2$ (**7**) that was isolated as colorless crystals in 80% yield. Compound **6** is an intermediate for forming **7** (Scheme 5). The ^{11}B and ^{31}P NMR spectra of **6** exhibited resonances at δ_B –7.1 and δ_P 3.0 ppm, respectively. These data compare well to those of $HCCP(Ph_2)\rightarrow B(C_6F_5)_3$ (δ_B –8.8 and δ_P 4.3 ppm) and $HCCP[(4\text{-}MeC_6H_4)_2]\rightarrow B(C_6F_5)_3$ (δ_B –9.9 and δ_P 4.1 ppm) measured at –60 °C.[21] Moreover, the ^{31}P resonance is close to that of the intermediate $Me_2HSiCCP(Ph_2)\rightarrow B(C_6F_5)_3$ (δ_P 4.3 ppm) detected at –70 °C.[15] These data suggest **6** a simple P→B coordination compound. The other NMR (δ_{SiH} 5.59, $\delta_{PC\equiv}$ 114.9 and $\delta_{SiC\equiv}$ 119.9 ppm, δ_{Si} –60.2 ppm) and IR ($\nu_{C\equiv C}$ 2124 and ν_{Si-H} 2190 cm^{-1}) data show difference from those of the precursor **3** due by the P→B bonding. Compound **7** was characterized to be an alkene with the C=C bond (1.341(4) Å; $\delta_{SiC=}$ 150.3 and $\delta_{BC=}$ 182.9 ppm) attached by four different groups C_6F_5 (δ_F –163.4, –157.2 and –138.2 ppm), $B(C_6F_5)_2$ (δ_B –3.9 and δ_F –163.7, –156.6 and –128.8 ppm), PPh_2 (δ_P 24.1 ppm), and $SiHMes_2$ (δ_{SiH} 5.32 and δ_{SiH} –50.7 ppm; ν_{Si-H} 2174 cm^{-1}) in an *E*-configuration (Figure 6). Compound **7** can be viewed also as a phosphaboracyclobutene due to a P–B bonding (2.033(4) Å), but the feature for arrangement of four groups around the C_2BP-ring is distinguished from that in **5**. To be reasoned, compound **7** is a result obtained from typical 1,1-carboboration reaction[22,23] while **5** is deviated from the self-hydrosilylation (*vide supra*).



Scheme 5. Reaction of **3** and $B(C_6F_5)_3$ to form **6** and **7**.

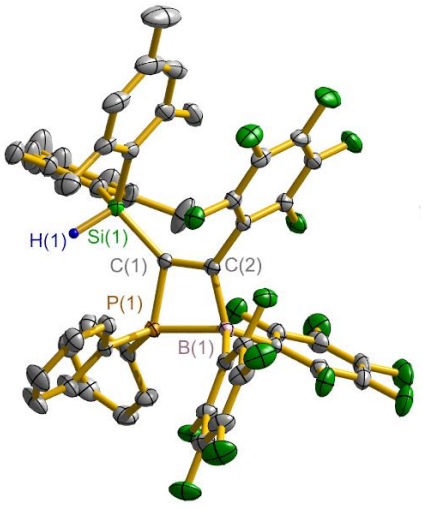
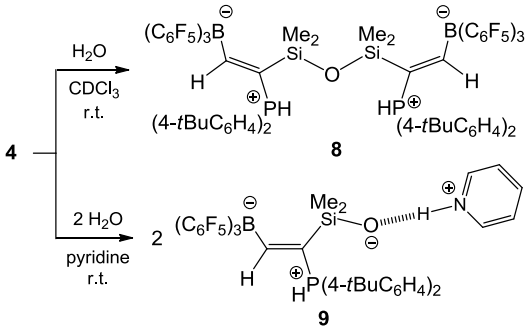


Figure 6. X-ray crystal structure of **7** with thermal ellipsoids at 30% probability level. H atoms except for that of the SiH are omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.341(4), C(1)–P(1) 1.808(4), C(1)–Si(1) 1.893(4), C(2)–B(1) 1.649(5), P(1)–B(1) 2.033(4), Si(1)–H(1) 1.34(4); C(2)–C(1)–Si(1) 137.3(3), C(2)–C(1)–P(1) 94.9(2), B(1)–C(2)–C(1) 108.1(3), P(1)–C(1)–Si(1) 126.0(2).

1,1-Carboboration reaction of $Me_3SiCCPMes_2$ with $B(C_6F_5)_2(CH_2CH_2PMes_2)$ has been known to produce at room temperature compound (*E*)-$Me_3Si(Mes_2P)CC(CH_2CH_2PMes_2)$-$B(C_6F_5)_2$, where two possibilities via the $(Mes_2PCH_2CH_2)(C_6F_5)_2B\text{-}PMes_2$ and $(Mes_2PCH_2CH_2)(C_6F_5)_2B\text{-}SiMe_3$ exchanges for further working exist.[23c] Also known is the reaction of *o*-$CCPPh_2C_6H_4CCSiMe_3$ and $B(C_6F_5)_3$ to form *o*-$C(PPh_2)C(C_6F_5)B(C_6F_5)_2C_6H_4CCSiMe_3$ at 60 °C, in which a prior reactivity was found at the $CCPPh_2$ directing to a $(C_6F_5)_3B\text{-}PPh_2$ change and then the 1,1-carboboration reaction.[24] Thus, we speculate that a further conversion of **6** into **7** is going through a $(C_6F_5)_3B\text{-}PPh_2$ exchange state for function rather than the $(C_6F_5)_3B\text{-}SiHMes_2$ one (Scheme 5).



Scheme 6. Reaction of **4** and H_2O to **8** and that of **4** and H_2O/pyridine to **9**.

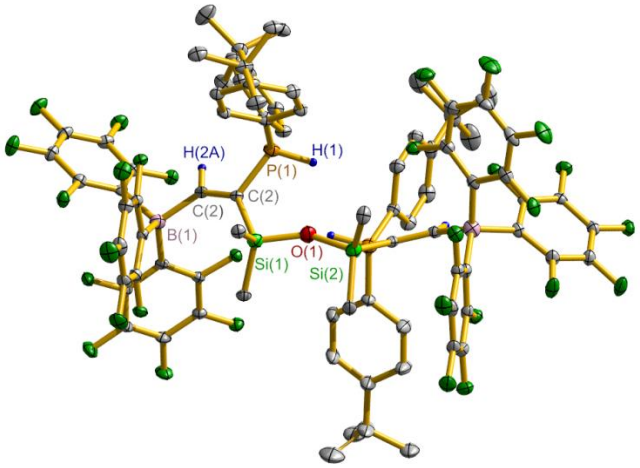


Figure 7. X-ray crystal structure of **8** with thermal ellipsoids at 30% probability level. H atoms except for those of =CH and PH are omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.355(4), C(2)–B(1) 1.646(6), C(1)–Si(1) 1.891(3), C(1)–P(1) 1.799(3), Si(1)–O(1) 1.648(2), P(1)–H(1) 1.33(3); C(2)–C(1)–Si(1) 131.4(2), C(2)–C(1)–P(1) 114.86(19), B(1)–C(2)–C(1) 131.9(2), P(1)–C(1)–Si(1) 113.75(14), C(1)–Si(1)–O(1) 101.00(11), Si(1)–O(1)–Si(2) 143.75(13).

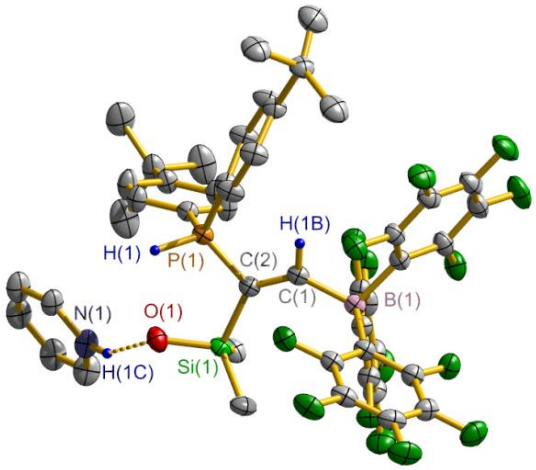
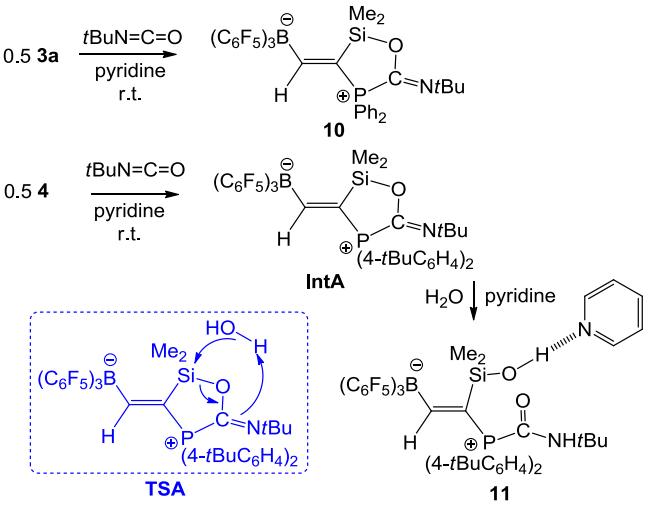


Figure 8. X-ray crystal structure of **9** with thermal ellipsoids at 20% probability level. H atoms except for those of the HC=, PH and NH are omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.349(3), C(1)–B(1) 1.642(4), C(2)–Si(1) 1.896(2), C(2)–P(1) 1.795(2), O(1)–Si(1) 1.645(2), P(1)–H(1) 1.36(3); C(2)–C(1)–B(1) 134.6(2), C(1)–C(2)–P(1) 115.33(17), C(1)–C(2)–Si(1) 132.21(19), Si(1)–C(2)–P(1) 112.43(12), C(2)–Si(1)–O(1) 103.19(11).

Compound **4** is a P/Si$^+$ LP and its reactivity towards small molecules of H_2O and/or isocyanate is investigated. The reaction of **4** and equivalent H_2O was carried out in $CDCl_3$ at room temperature and generated compound [(*E*)-$(C_6F_5)_3$BCHC[PH(4-*t*Bu$C_6H_4)_2$]Si(Me_2)]$_2$(μ-O) (**8**, colorless crystals, 80% yield, Figure 7). When this reaction was conducted in the pyridine donor solvent instead of $CDCl_3$, compound (*E*)-$(C_6F_5)_3$BCHC[PH(4-*t*Bu$C_6H_4)_2$]Si(Me_2)O(HNC_5H_5) (**9**, colorless crystals, 60% yield, Figure 8) was yielded (Scheme 6). The reaction mechanism has been previously discussed,[15] which involved a disassociation of H_2O by the P/Si$^+$ LP, owning to the concerted silylium's electrophilic and P-donor's nucleophilic interactions. Noted is the disclosure of compound **9**, which may reveal an intermediate reaction because of the pyridine stabilization of the (*E*)-$(C_6F_5)_3$BCHC[PH(4-*t*Bu$C_6H_4)_2$]Si(Me_2)OH species. X-ray crystallographic study indicated that final structural refinements converged to an σ-bonded NH group more stable than the σ-bonded OH group. Then, the data by O···H separation of 2.107 Å (av), H–N bond length of 0.86 Å, and O···H–N bond angle of 157.8° (av) confirmed cleanly a hydrogen bonding located within the SiO···H–NC_5H_5 part.

We further carried out reactions using **4** and the previously prepared **3a** each with isocyanate *t*BuNCO. Reaction of **3a** and *t*BuNCO was conducted in pyridine at room temperature and afforded smoothly compound [$(C_6F_5)_3$BHC]CSi(Me_2)P(Ph_2)OC(N*t*Bu) (**10**, colorless crystals, 46% yield). The reaction of **4** with *t*BuNCO was performed as well in pyridine at room temperature. After reaction, a standing of the solution top-layered with *n*-hexane at –20 °C for crystallization, however, gave compound (*E*)-$(F_5C_6)_3$BCHC[P(4-*t*Bu$C_6H_4)_2$C(O)NH*t*Bu]-[Si(Me_2)OH(NC_5H_5)] (**11**), a further H_2O-dissociation species. This is probably due to penetration of H_2O in the course of crystallization of the product. Nevertheless, we repeated the reaction of **4** with *t*BuNCO and then stoichiometric H_2O and obtained eventually compound **11** (colorless crystals, 45% yield) (Scheme 7). The reactions of the FLP complexes with isocyanates have been reported for a few, which showed two activation routes at the respective C=O and N=C bonds of the isocyanate.[25] The formation of **10** indicates a result by the P/Si$^+$ LP reaction selectively at the C=O bond to give a C_2OPSi-five membered heterocycle. The generation of compound **11** followed a way similar to **10**, leading to similar C_2OPSi-cycle [$(C_6F_5)_3$BHC]CSi(Me_2)P[(4-*t*Bu$C_6H_4)_2$]OC(N*t*Bu) (**IntA**), and **IntA** further cleaved H_2O under the C_2OPSi-ring opening (**TSA**). This shows a way uniquely to the P-bonded acylamine molecules.



Scheme 7. Reaction of **3a** and *t*BuNCO to **10** and that of **4** and *t*BuNCO and H_2O to **11**.

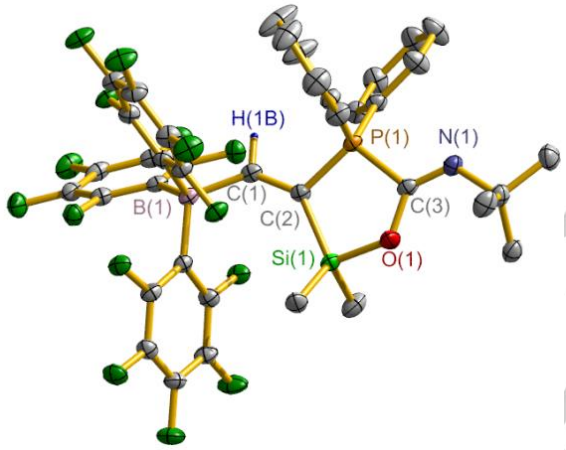


Figure 9. X-ray crystal structure of **10** with thermal ellipsoids at 50% probability level. H atoms except for that of the HC= are omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.351(3), C(1)–B(1) 1.620(3), C(2)–Si(1) 1.892(2), C(2)–P(1) 1.789(2), P(1)–C(3) 1.834(1), O(1)–C(3) 1.356(2), O(1)–Si(1) 1.7025(16), C(3)–N(1) 1.248(3); Si(1)–C(2)–P(1) 106.11(10), C(2)–P(1)–C(3) 101.20(9), P(1)–C(3)–O(1) 111.36(14), C(3)–O(1)–Si(1) 121.16(13), O(1)–Si(1)–C(2) 98.57(8).

X-ray crystallographic study of **10** clearly discloses the C_2OPSi-heterocycle nature (Figure 9). The C–O bond length inside the cycle is 1.356(2) Å and the C–N bond length outside is 1.248(3) Å. Both these two bond lengths compare a little longer than those in isocyanate.[26] It is noted that the C–O bond distance is a little shorter than that of the formal single bond, moreover the C−N bond length compares shorter than that of the double bond. Therefore, these data indicate a yet electronic conjugation over the O–C=N part after a [3+2] polar cycloaddition. Compound **10** is still an intramolecular zwitterion with the negative charge located at the B atom outside but the positive charge at the P center inside the C_2OPSi-ring. X-ray structure of **11** confirms feature of the PC(O)NH*t*Bu (P–C 1.8861(18), C–O 1.220(2), C–N 1.342(2) Å) and SiO–H···NC_5H_5 (Si–O 1.6290(12), O–H 0.81(3), H···N 1.916(3) Å, O–H···N 161.4°) moieties as a result by the further reaction of the C_2OPSi-cycle **IntA** with H_2O (Figure 10). The pyridine molecule behaves well again as a stabilizer for forming the hydrogen bonding with the SiOH group.

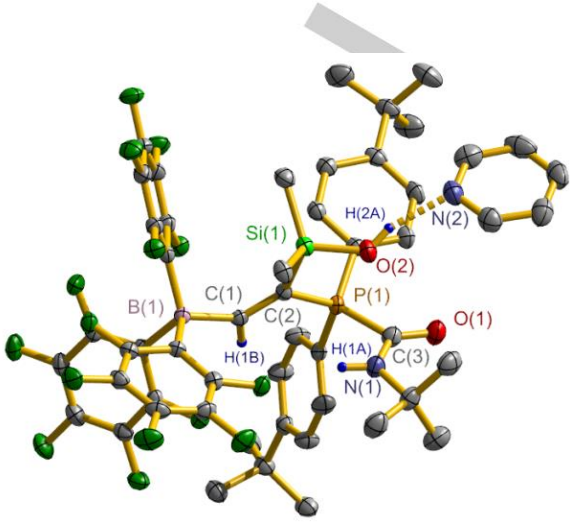


Figure 10. X-ray crystal structure of **11** with thermal ellipsoids at 50% probability level. H atoms except for those of the HC=, NH, and OH are omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.351(2), C(1)–B(1) 1.638(2), C(2)–Si(1) 1.9027(16), C(2)–P(1) 1.7954(15), Si(1)–O(2) 1.6290(12), P(1)–C(3) 1.8861(18), C(3)–O(1) 1.220(2), C(3)–N(1) 1.342(2), O(2)–H(2A) 0.81(3), N(2)···H(2A) 1.916(3); C(1)–C(2)–Si(1) 132.70(12), C(1)–C(2)–P(1) 116.20(11), B(1)–C(1)–C(2) 132.41(14), P(1)–C(2)–Si(1) 110.91(8), C(2)–Si(1)–O(2) 100.66(7), C(2)–P(1)–C(3) 110.30(7), P(1)–C(3)–O(1) 119.60(13), P(1)–C(3)–N(1) 112.91(12).

Conclusion

In summary, by the C≡C-centered, three-folded substituent transformation, phosphanylhydrosilylalkynes $R_2HSiCCPAr_2$ (R,Ar: Me,4-*t*BuC_6H_4 **1**, Me,Mes **2**, Mes,Ph **3**) have been prepared. The NMR spectral data indicate a distinguished property of the phosphanylhydrosilylalkyne with substitution of either the $SiHMes_2$ (in **2**) or $PMes_2$ (in **3**) group. Therefore, the reaction of **1** and $B(C_6F_5)_3$ yielded *E*-alkene dimer **4** although isolation of another compound was not successful. This reaction proceeded through a $B(C_6F_5)_3$-$SiHMe_2$ exchange generating the $[SiHMe_2]^+$ for self-hydrosilylation. The reaction of **2** and $B(C_6F_5)_3$ gave *Z*-alkene C_2BP-heterocycle **5**, which went through a $B(C_6F_5)_3$-$PMes_2$ exchange rendering a phosphacyclopropene for function, showing a new self-hydrosilylation way. Furthermore, the reaction of **3** and $B(C_6F_5)_3$ afforded *E*-alkene C_2BP-heterocycle **7** at elevated temperature. This is probably a result by a $B(C_6F_5)_3$-PPh_2 exchange to form $[PPh_2]^+$ conducting 1,1-carboboration. All of these results reveal diverse reaction patterns of the phosphanylhydrosilylalkynes due to variation of either hydrosilyl or phosphanyl substituent. Of particular attention is the Mes group substitution at either the Si or P nucleus. Furthermore, reactions using **4** and the previously prepared **3a** both as the P/Si^+ LP toward H_2O and/or *t*BuNCO were accomplished, which afforded novel H_2O-dissociation and/or *t*BuNCO-cycloaddition compounds.

Experimental Section

Materials and Methods All manipulations were carried out under dry argon or nitrogen atmosphere by using Schlenk line and glovebox techniques. Organic solvents toluene, *n*-hexane and diethyl ether were dried by refluxing with sodium/potassium benzophenone under N_2 prior to use. NMR (^{1}H, ^{11}B, ^{13}C, ^{19}F, ^{29}Si, and ^{31}P) spectra were recorded on Bruker Avance II 400 or 500 Spectrometer. Melting point of compound was measured in a sealed glass tube using the Büchi-540 instrument. Elemental analysis was performed on a Thermo Quest Italia SPA EA 1110 instrument. Commercial reagents were purchased from Energy Chemical and J&K Chemical Co. and used as received. Compounds Mes_2SiHCl,[27] Ar_2PCCH (Ar = Ph, 2,4,6-$Me_3C_6H_2$, 4-*t*BuC_6H_4),[21,28] $B(C_6F_5)_3$,[29] and [(*E*)-$(C_6F_5)_3BCHC(PPh_2)SiMe_2]_2$ (**3a**)[15] were prepared by referencing to literatures.

$Me_2HSiCCP(4\text{-}tBuC_6H_4)_2$ (1) At –78 °C, *n*BuLi (5.30 mL, 2.4 M *n*-hexane solution, 12.5 mmol) was added dropwise to a stirring solution of (4-*t*$BuC_6H_4)_2PCCH$ (4.05 g, 12.5 mmol) in Et_2O (80 mL). The mixture was left to warm to room temperature and kept stirring for additional 6 h. And then this reaction mixture was cooled again to –78 °C and to it a little excess of Me_2SiHCl (1.4 mL, 12.6 mmol) was added. The mixture was left to warm to room temperature and kept stirring for additional 12 h. After the reaction, the LiCl generated was filtered off and the filtrate was evaporated to dryness. The residue was washed with cold *n*-hexane (–20 °C, 2 mL) and then dried in vacuum to give **1** as an off-white solid. Yield: 4.06 g (85%). Mp: 96 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = 0.32 (d, $^3J_{HH}$ = 3.8 Hz, 6 H, Si*Me*), 1.31 (s, 18 H, *tBu*), 4.24 (ds, $^3J_{HH}$ = 3.8 Hz, J_{PH} = 1.2 Hz, 1 H, Si*H*), 7.38 (m, 4 H), 7.55 (m, 4 H) (C_6H_4). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K, ppm): δ = –2.9 (Si*Me*), 31.4 (*CMe*$_3$), 34.7 (*C*Me$_3$), 106.0 (d, J_{PC} = 15.1 Hz, P*C*≡), 112.7 (d, J_{PC} = 3.0 Hz, Si*C*≡), 125.7 (d, J_{PC} = 7.9 Hz), 132.4 (d, J_{PC} = 5.2 Hz), 132.5 (d, J_{PC} = 21.2 Hz), 152.1 (*C*$_6$H$_4$). ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, 298 K, ppm): δ = –37.6. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K, ppm): δ = –35.6. IR (KBr plate, cm^{-1}): *v* = 2104 (C≡C), 2141 (Si–H). Anal. calcd (%) for $C_{24}H_{33}PSi$ (M_r = 380.59): C 75.74, H 8.74. Found: C 75.65, H 8.66.

$Me_2HSiCCPMes_2$ (2) At –78 °C, *n*BuLi (2.30 mL, 2.4 M *n*-hexane solution, 5.40 mmol) was added dropwise to a stirring solution of Mes_2PCCH (1.75 g, 5.40 mmol) in Et_2O (60 mL). The mixture was left to warm to room temperature and kept stirring for additional 6 h. And then the reaction mixture was cooled again to –78 °C and to it a little excess of Me_2SiHCl (0.6 mL, 5.70 mmol) was added. The mixture was left to warm to room temperature and kept stirring for additional 12 h. After the reaction, the LiCl generated was filtered off and the filtrate was evaporated to dryness. The residue was extracted with *n*-hexane and the extract was dried in vacuum to give **2** as an orange solid. Yield: 1.33 g (71%). Mp: 56 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = 0.22 (d, $^3J_{HH}$ = 3.8 Hz, 6 H, Si*Me*), 2.25 (s, 6 H, *p-Me*), 2.38 (s, 12 H, *o-Me*), 4.12 (ds, $^3J_{HH}$ = 3.8 Hz, J_{PH} = 1.5 Hz, 1 H, Si*H*), 6.80 (m, 4 H, C_6H_2). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K, ppm): δ = –3.3 (Si*Me*), 21.0 (*p-Me*), 23.1 and 23.2 (*o-Me*), 106.8 (d, J_{PC} =16.8 Hz, P*C*≡), 112.8 (Si*C*≡), 129.2 (d, J_{PC} = 11.4 Hz), 130.0 (d, J_{PC} = 3.6 Hz), 138.4, 142.2 (d, J_{PC} = 15.6 Hz) (C_6H_2). ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, 298 K, ppm): δ = –38.1. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K, ppm): δ = –54.7. IR (KBr plate, cm^{-1}): *v* = 2086 (C≡C), 2126 (Si–H). Anal. calcd (%) for $C_{22}H_{29}PSi$ (M_r = 352.52): C 74.96, H 8.29. Found: C 74.80, H 8.33.

$Mes_2HSiCCPPh_2$ (3) At –78 °C, *n*BuLi (2.2 mL, 2.4 M *n*-hexane solution, 5.20 mmol) was added dropwise to a stirring solution of Ph_2PCCH (1.09 g, 5.20 mmol) in Et_2O (50 mL). The mixture was left to warm to room temperature and kept stirring for additional 6 h. And then the reaction mixture was cooled again to –78 °C and to it a solution of Mes_2SiHCl (1.57 g, 5.20 mmol) in Et_2O (15 mL) was added. The mixture was left to warm to room temperature and kept stirring for additional 12 h. After the reaction, the LiCl generated was filtered off and the filtrate was evaporated to dryness. The residue was extracted with *n*-hexane and the extract was dried in vacuum to give **3** as a slight-grey solid. Yield: 1.86 g (75%). Mp: 88 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = 2.27 (s, 6 H, *p-Me*), 2.42 (s, 12 H, *o-Me*), 5.62 (s, 1 H, Si*H*), 6.83 (m, 4 H, C_6H_2), 7.31 (m, 6 H), 7.55 (m, 4 H) (*Ph*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K, ppm): δ = 21.2 (*p-Me*), 23.7 (*o-Me*), 107.2 (d, J_{PC} =15.2 Hz, P*C*≡), 113.2 (d, J_{PC} = 3.2 Hz, Si*C*≡), 127.4, 129.1, 139.8, 144.8 (C_6H_2), 128.7 (d, J_{PC} = 7.5 Hz), 132.7, 132.9, 135.7 (d, J_{PC} = 6.2 Hz) (*Ph*). ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, 298 K, ppm): δ = –61.1. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K, ppm): δ = –31.5. IR (KBr plate, cm^{-1}): *v* = 2091 (C≡C), 2148 (Si–H). Anal. calcd (%) for $C_{32}H_{33}PSi$ (M_r = 476.66): C 80.63, H 6.98. Found: C 80.57, H 6.92.

{(*E*)-$(C_6F_5)_3BCHC[P(4\text{-}tBuC_6H_4)_2]SiMe_2\}_2$ (4) A solution of **1** (0.38 g, 1 mmol) and $B(C_6F_5)_3$ (0.51 g, 1 mmol) in toluene (20 mL) was stirred at room temperature. After 1.5 h, compound **4** started to precipitate from the solution. After stirring for additional 10.5 h, *n*-hexane (30 mL) was added till no more precipitates were generated. Compound **4** was collected by filtration and dried in vacuum. Yield: 0.31 g (35%). Mp: 277 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = 0.0 (d, J_{PH} = 8.0 Hz, 6 H, Si*Me*), 1.4 (s, 18 H, *tBu*), 7.33 (m, 4 H), 7.56 (m, 4 H) (C_6H_4), 9.32 (d, J_{PH} = 48.7 Hz, 1 H, *H*C=). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$, 298 K, pp m): δ = –14.8. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 298 K, ppm): δ = –164.3 (m, 6 F, *m-F*), –158.8 (m, 3 F, *p-F*), –128.2 (m, 6 F, *o-F*). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K, ppm): δ = 2.2. The ^{13}C and ^{29}Si NMR data were not obtained due to a not good solubility of **4**. Anal. calcd (%) for $C_{84}H_{66}B_2F_{30}P_2Si_2$ (M_r = 1785.12): C 56.52, H 3.73. Found: C 56.55, H 3.71. X-ray quality single-crystals of **4** were obtained from its $CDCl_3$ solution after keeping undisturbedly at room temperature for 12 h.

(*Z*)-$(C_6F_5)_2BCHC(PMes_2)SiMe_2(C_6F_5)$ (5) At room temperature, a solution of **2** (0.353 g, 1.0 mmol) in toluene (10 mL) was slowly added to a solution of $B(C_6F_5)_3$ (0.512 g, 1.0 mmol) in toluene (10 mL). During addition, a color change promptly to red and then dark-red was observed. After addition, the mixture was stirred for two days and finally an almost colorless solution was developed. The toluene solvent was removed under reduced pressure and the residue was extracted with *n*-hexane (10 mL). The extract was kept at –20 °C. 72 h later, colorless crystals of **5** were formed. Yield: 0.48 g (55%). Mp: 168 °C (decomposed). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = 0.51 (d, J_{PH} = 1.9 Hz, 3 H) and 0.52 (d, J_{PH} = 1.9 Hz, 3 H) (Si*Me*), 2.0 (s, 12 H, *o-Me*), 2.2 (s, 6 H, *p-Me*), 6.7 (m, 4 H, C_6H_2), 8.68 (d, J_{PH} = 110.0 Hz, 1 H, *H*C=). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K, ppm): δ = –0.03 (m, Si*Me*), 20.7 (*p-Me*), 23.2, 23.3 (*o-Me*), 125.2 (d, J_{PC} = 27.9 Hz, Si*C*=), 130.5 (d, J_{PC} = 8.1 Hz), 141.1 (d, J_{PC} = 8.2 Hz), 141.2 (d, J_{PC} = 2.4 Hz), 143.0 (d, J_{PC} = 25.5 Hz) (C_6H_2), 108.3 (m), 117.3 (br), 135.8 (br), 138.3 (br), 139.0 (br), 141.5 (br), 143.6 (br), 146.1 (br), 147.8 (br), 148.5 (br), 150.4 (br) (C_6F_5), 188.8 (br, B*C*=). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$, 298 K, ppm): δ = –3.9. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 298 K, ppm): δ = –163.9 (m, 4 F, *m-F*), –157.3 (m, 2 F, *p-F*), –125.2 (m, 4 F, *o-F*) (BC_6F_5), –161.1 (m, 2 F, *m-F*), –151.0 (m, 1 F, *p-F*), –125.2 (m, 2 F, *o-F*) (SiC_6F_5). ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, 298 K, ppm): δ = –13.3. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K, ppm): δ = 24.3. Anal. calcd (%) for $C_{40}H_{29}BF_{15}PSi$ (M_r = 864.50): C 55.57, H 3.38. Found: C 55.59, H 3.34.

$Mes_2HSiCCP(Ph_2)B(C_6F_5)_3$ (6) At room temperature, to the NMR tube was added **3** (0.048 g, 0.1 mmol), $B(C_6F_5)_3$ (0.051 g, 0.1 mmol) and $CDCl_3$ (0.4 mL). A slight-yellow solution was developed, and compound **6** was formed as indicated upon analysis by the combined ^{1}H, ^{13}C, ^{11}B, ^{19}F, ^{29}Si and ^{31}P spectra. After removal of $CDCl_3$, compound **6** was obtained as colorless oil. Yield: 100% on the basis of the NMR spectral analysis. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = 2.34 (br, 18 H, *p-Me* and *o-Me*), 5.59 (s, 1 H, Si*H*), 6.88 (m, 4 H, C_6H_2), 7.34–7.39 (m, 6 H), 7.51–7.56 (m, 4 H) (*Ph*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K, ppm): δ = 21.1 (*p-Me*), 23.3 (*o-Me*), 114.9 (P*C*≡), 119.9 (Si*C*≡), 125.0, 128.7 (d, J_{PC} = 10.5 Hz), 129.1, 131.7, 133.0 (d, J_{PC} = 10.8 Hz), 139.0, 147.3 (*Ph* and C_6H_2), 135.8 (br), 138.2 (br), 139.0 (br), 141.5 (br), 147.3 (br), 149.7 (br) (C_6F_5). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$, 298 K, ppm): δ = –7.1. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 298 K, ppm): δ = –163.9 (m, 6 F, *m-F*), –155.0 (m, 6 F, *p-F*), –126.9 (m, 4 F, *o-F*). ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, 298 K, ppm): δ = –60.2. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K, ppm): δ = 3.0. IR (KBr plate, cm^{-1}): *v* = 2124 (C≡C), 2190 (Si–H). Anal. calcd (%) for $C_{50}H_{33}BF_{15}PSi$ (M_r = 988.66): C 60.74, H 3.36. Found: C 60.82, H 3.75.

$Mes_2HSi(Ph_2P)CC(C_6F_5)B(C_6F_5)_2$ (7) A solution of **3** (0.48 g, 1 mmol) and $B(C_6F_5)_3$ (0.51 g, 1 mmol) in toluene (10 mL) was heated at 100 °C for two days. After cooling to room temperature, the solution was concentrated to ca. 4 mL and to it *n*-hexane (4 mL) was added. This solution mixture was kept at –20 °C. 72 h later, colorless crystals of **7** were generated. Yield: 0.79 g (80%). Mp: 187 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = 2.12 (s, 12 H, *o-Me*), 2.23 (s, 6 H, *p-Me*), 5.32 (d, J_{PH} = 1.8 Hz, 1 H, Si*H*), 6.67 (s, 4 H, C_6H_2), 7.27–7.31 (m, 4 H), 7.34–7.39 (m, 4 H), 7.47–7.52 (m, 2 H) (*Ph*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K, ppm): δ = 21.1 (*p-Me*), 23.7 (*o-Me*), 126.0 (d, J_{PC} = 42.0 Hz), 126.6 (d, J_{PC} = 2.6 Hz), 128.7 (d, J_{PC} = 10.5 Hz), 128.9, 132.1 (d, J_{PC} = 2.7 Hz), 133.0 (d, J_{PC} = 9.2 Hz), 140.3, 145.0 (*Ph* and C_6H_2), 150.3 (d, J_{PC} = 22.3 Hz) (Si*C*=), 135.8 (br), 138.3 (br), 138.8 (br), 141.3 (br), 143.6 (br), 146.3 (br), 148.7 (br) (C_6F_5), 182.9 (B*C*=). ^{11}B{^{1}H} NMR (128 MHz,

$CDCl_3$, 298 K, ppm): δ = –3.9. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, 298 K, ppm): δ = –163.7 (m, 4 F, *m-F*), –156.6 (m, 2 F, *p-F*), –128.8 (m, 4 F, *o-F*) (BC_6F_5), –163.4 (m, 2 F, *m-F*), –157.2 (m, 1 F, *p-F*), –138.2 (m, 2 F, *o-F*) (CC_6F_5). $^{29}Si\{^1H\}$ NMR (79 MHz, $CDCl_3$, 298 K, ppm): δ = –50.7. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K, ppm): δ = 24.1. IR (KBr plate, cm^{-1}): ν = 2174 (Si–H). Anal. calcd (%) for $C_{50}H_{33}BF_{15}PSi$ (M_r = 988.66): C 60.74, H 3.36. Found: C 60.64, H 3.28.

{(*E*)-$(C_6F_5)_3$BCHC[PH(4-*t*BuC_6H_4)$_2$]Si(Me_2)}$_2$(μ-O) (8) At room temperature, H_2O (0.001 g, 0.05 mmol) was added to a solution of **4** (0.089 g, 0.05 mmol) in $CDCl_3$ (0.4 mL). The mixture was kept at room temperature. 48 h later, colorless crystals of **8** were generated. Yield: 0.082 g (90%). Mp: 160 °C. ^1H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = –0.35 (s, 6 H, Si*Me*), 1.35 (s, 18 H, *tBu*), 7.45 (d, J_{PH} = 463.4 Hz, 1 H, P*H*), 7.39 (m, 4 H), 7.65 (m, 4 H) (C_6H_4), 8.71 (d, J_{PH} = 57.5 Hz, 1 H, *H*C=). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 298 K, ppm): δ = 2.0 (Si*Me*), 31.0 (C*Me*$_3$), 35.7 (C*Me*$_3$), 113.5 (d, J_{PC} = 86.6 Hz, Si*C*=), 125.5, 127.7 (d, J_{PC} = 13.0 Hz), 128.4, 129.2, 133.8 (d, J_{PC} =10.4 Hz), 160.0 (C_6H_4), 115.8 (br), 116.1(br), 135.7 (br), 138.0 (br), 140.3 (br), 138.1 (br), 140.4 (br), 146.9 (br), 149.4 (br) (C_6F_5), 208.1 (br, B*C*=). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$, 298 K, ppm): δ = –15.4 (br). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, 298 K, ppm): δ = –165.0 (m, 6 F, *m-F*), –160.0 (m, 3 F, *p-F*), –130.2 (m, 6 F, *o-F*). $^{29}Si\{^1H\}$ NMR (79 MHz, $CDCl_3$, 298 K, ppm): δ = 5.1. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K, ppm): δ = 6.7. IR (KBr plate, cm^{-1}): ν = 1989 (P–H). Anal. calcd (%) for $C_{84}H_{68}B_2F_{30}OP_2Si_2$ (M_r = 1803.13): C 55.95, H 3.80. Found: C 56.03, H 3.82.

(*E*)-$(C_6F_5)_3$BCHC[PH(*t*BuC_6H_4)$_2$]Si(Me_2)O(HNC_5H_5) (9) At room temperature, to a solution of **4** (0.35 g, 0.19 mmol) in pyridine (6 mL) was added H_2O (0.007 g, 0.39 mmol). The mixture was stirred to give a solution. The solvent was removed in vacuum and the residue was dissolved in toluene/*n*-hexane (2 mL/2 mL) mixture. The solution was kept at –20 °C for 24 h, generating colorless crystals of **9**. Yield: 0.23 g (60%). Mp: 167 °C (decomposed). ^1H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = –0.21 (s, 6 H, Si*Me*), 1.35 (s, 18 H, *tBu*), 3.66 (br, 1 H, N*H*), 7.29 (m, 2 H), 7.69 (m, 1 H), 8.47 (m, 2 H) (NC_5H_5), 7.48 (m, 4 H), 7.62 (m, 4 H) (C_6H_4), 7.87 (d, J_{PH} = 58.9 Hz, 1 H, P*H*), 8.63 (d, J_{PH} = 58.9 Hz, 1 H, *H*C=). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 298 K, ppm): δ = 0.9 (Si*Me*), 30.9 (C*Me*$_3$), 35.5 (C*Me*$_3$), 117.7 (d, J_{PC} = 85.7 Hz, Si*C*=), 127.2 (d, J_{PC} = 12.8 Hz), 128.4, 129.2, 133.6 (d, J_{PC} =10.1 Hz), 158.8 (C_6H_4), 124.5, 137.0, 148.8 (NC_5H_5), 119.4 (m), 135.6 (m), 138.2 (m), 140.1 (m), 147.2 (br), 149.5 (br) (C_6F_5), 204.7 (br, B*C*=). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$, 298 K, ppm): δ = –15.3 (br). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, 298 K, ppm): δ = –165.5 (m, 6 F, *m-F*), –160.7 (m, 3 F, *p-F*), –130.4 (m, 6 F, *o-F*). $^{29}Si\{^1H\}$ NMR (79 MHz, $CDCl_3$, 298 K, ppm): δ = 5.8. $^{31}P\{^1H\}$ NMR (162 MHz, CCl_3, 298 K, ppm): δ = 11.4. IR (KBr plate, cm^{-1}): ν = 2963 (N–H), 1935 (P–H). Anal. calcd (%) for $C_{47}H_{40}BF_{15}NOPSi$ (M_r = 989.67): C 57.04, H 4.07, N 1.42. Found: C 57.01, H 4.05, N 1.43.

[$(C_6F_5)_3$BHC]CSi(Me_2)P(Ph_2)OC(N*t*Bu) (10) At room temperature, *t*BuNCO (0.052 g, 0.52 mmol) was added to a solution of **3a** (0.41 g, 0.26 mmol) in pyridine (6 mL). The mixture was stirred for 4 h. All volatiles were removed in vacuum and the residue was dissolved in toluene/*n*-hexane (2 mL/2 mL) mixture. The solution was kept at –20 °C for 24 h, generating colorless crystals of **10**. Yield: 0.21 g (46%). ^1H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = –0.08 (s, 6 H, Si*Me*), 1.32 (s, 18 H, *tBu*), 7.64 (m, 8 H) (C_6H_4), 8.80 (d, J_{PH} = 42.8 Hz , 1 H, *H*C=). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$, 298 K, ppm): δ = –14.6. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, 298 K, ppm): δ = –164.7.0 (m, 6 F, *m-F*), –159.9 (m, 3 F, *p-F*), –130.5 (m, 6 F, *o-F*). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K, ppm): δ = 5.0. The ^{13}C and ^{29}Si NMR spectra were not measured. Anal. calcd (%) for $C_{39}H_{26}BF_{15}NOPSi$ (M_r = 879.48): C 53.26, H 2.98, N 1.59. Found: C 53.27, H 3.02, N 1.61.

(*E*)-$(F_5C_6)_3$BCHC[P(4-*t*BuC_6H_4)$_2$C(O)NH*t*Bu][Si(Me_2)OH(NC_5H_5)] (11) At room temperature, *t*BuNCO (0.02 g, 0.20 mmol) was added to a solution of **4** (0.179 g, 0.10 mmol) in pyridine (6 mL). The mixture was stirred at room temperature for 4 h. Then to the solution H_2O (0.0036 g, 0.20 mmol) was added. The mixture was stirred for 4 h. The volatiles were removed in vacuum and the residue was dissolved in toluene/*n*-hexane (2 mL/2 mL). The solution was kept at –20 °C for 48 h, generating colorless crystals of **11**. Yield: 0.098 g (45%). Mp: 120 °C. ^1H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = –0.17 (s, 6 H, Si*Me*), 1.33 (s, 18 H, *tBu*), 1.54 (s, 9 H, *tBu*), 2.58 (s, 1 H, N*H*), 6.87 (br, 1 H, SiO*H*), 7.28 (m, 1 H), 7.68 (m, 2 H), 8.51 (m, 2 H) (NC_5H_5), 7.60 (m, 8 H) (C_6H_4), 8.74 (d, J_{PH} = 55.1 Hz , 1 H, *H*C=). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 298 K, ppm): δ = 1.9 (Si*Me*), 28.5 (C*Me*$_3$), 31.0 (C*Me*$_3$), 31.8 (C*Me*$_3$), 35.5 (C*Me*$_3$), 116.4 (d, J_{PC} = 83.1 Hz, Si*C*=), 123.9, 136.3, 149.7 (NC_5H_5), 127.0 (d, J_{PC} =12.3 Hz), 133.8 (d, J_{PC} =8.8 Hz), 158.7 (C_6H_4), 120.8 (m), 135.6 (m), 138.1 (m), 138.0 (m), 140.4 (m), 147.2 (m), 149.6 (br) (C_6F_5), 162.5 (d, J_{PC} = 95.6 Hz, *C*=O), 210.7 (br, B*C*=). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$, 298 K, ppm): δ = –21.7. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, 298 K, ppm): δ = –165.0 (m, 6 F, *m-F*), –160.3 (m, 3 F, *p-F*), –130.5 (m, 6 F, *o-F*). $^{29}Si\{^1H\}$ NMR (79 MHz, $CDCl_3$, 298 K, ppm): δ = 8.0. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K, ppm): δ = 17.3. IR (KBr plate, cm^{-1}): ν = 3702 (O–H), 2912 (N–H). Anal. calcd (%) for $C_{52}H_{49}BF_{15}N_2O_2PSi$ (M_r = 1088.80): C 57.36, H 4.54, N 2.57. Found: C 57.31, H 4.50, N 2.54.

X-Ray Crystallographic Analysis Crystallographic data for compounds **2**, **4**$_{0.5}$·0.5 toluene·*n*-hexane, **5**, **7**·toluene, **8**·2 $CDCl_3$, **9**·C_6D_6, **10**·0.5 *n*-hexane and **11**·0.5 *n*-hexane were collected on a Rigaku Oxford Diffraction system. During measurements a graphite-monochromatic Cu-*K*a radiation (λ= 1.54178 Å) was applied for **4**$_{0.5}$·0.5 toluene·*n*-hexane, **8**·2 $CDCl_3$, **9**·C_6D_6, **10**·0.5 *n*-hexane and **11**·0.5 *n*-hexane and the Mo-*K*a radiation (λ = 0.71073 Å) was used for **1**, **5** and **7**·toluene. Absorption corrections were all employed using the spherical harmonics program (multi-scan type). All the structures were solved by direct methods (SHELXS-96)[30] and refined against F2 using SHELXL-2014.[31] In general, the non-hydrogen atoms were located by difference Fourier synthesis and refined anisotropically, and hydrogen atoms were included using a riding mode with U_{iso} tied to the U_{iso} of the parent atoms unless otherwise specified. In **2**, the $SiHMe_2$ group was disordered and treated by PART method, in which Si(1)H(1)C(3)C(4) and Si(1A)H(1A)C(3A)C(4A) were located and refined in the respective occupancies of 0.78283 and 0.21717. The H(1) and H(1A) atoms were located by difference Fourier synthesis and refined isotropically. In **4**$_{0.5}$·0.5 toluene·*n*-hexane, a half moiety of **4** was disclosed and the whole molecule was obtained *via* the symmetric operation. The 0.5 toluene molecule was seriously disordered, which was treated by PART method and refined to give two parts. The hydrogen atoms in these two parts were not able to be added. In **7**·toluene, the SiH hydrogen atom was located by difference Fourier synthesis and refined isotropically. The toluene molecule was disordered, which was treated by PART method and refined into two parts C(61)C(62)C(63)C(64)C(65)C(66)C(67) and C(61A)C(62A)-C(63A)C(64A)C(65A)C(66A)C(67A) with the respective occupancies of 0.45743 and 0.54257. In **8**·2 $CDCl_3$, both two $CDCl_3$ molecules were disordered and treated by PART method. One molecule was refined into two parts C(85)Cl(1)Cl(2)Cl(3) and C(85A)Cl(1A)Cl(2A)Cl(3A) with the respective occupancies of 0.67610 and 0.32390 and another into C(86)Cl(4)Cl(5)Cl(6) and C(86A)Cl(4A)Cl(5A)Cl(6A) with the respective occupancies of 0.74841 and 0.25159. The three methyl groups of one *t*Bu were also disordered and treated by PART method refining into C(54)C(55)C(56) and C(54A)C(55A)C(56A) with the respective occupancies of 0.52062 and 0.47938. In addition, each H atom of the two PH moieties was located by difference Fourier synthesis and refined isotropically. In **9**·C_6D_6, two halves of the C_6D_6 molecules were disclosed, of which one half molecule was seriously disordered. The carbon atoms in this molecule were refined isotropically and to which the hydrogen atoms were not able to be added. The pyridine molecule was disordered and treated by PART method refining into N(1)C(43)C(44)-C(45)C(46)C(47) and N(1A)C(43A)C(44A)C(45A)C(46A)-C(47A) with the respective occupancies of 0.59649 and 0.40351. One *t*Bu group was disordered and treated by PART method refining into C(11)C(12)C(13)C(14) and C(11A)C(12A)C(13A)C(14A) with the respective occupancies of 0.57195 and 0.42805. Three methyl groups of the other *t*Bu were disordered and treated by PART method refining into C(22)C(23)C(24) and C(22A)C(23A)C(24A) with the respective occupancies of 0.17963 and 0.82037. The PH hydrogen atom was located by difference Fourier synthesis and refined isotropically. The H atom existed within hydrogen bonding of the SiO···H–NC_5H_5 part was refined to bond to the N atom rather than the O atom. In **10**·0.5 *n*-hexane, the half *n*-hexane molecule was disordered and treated by PART method refining into C(41)C(42)C(43) and C(41A)C(42A)C(43A) with the respective occupancies of 0.48647 and 0.51353. In **11**·0.5 *n*-hexane, the half *n*-hexane molecule was disordered and treated by PART method refining into C(53)C(54)C(55) and C(53A)C(54A)C(55A) with the respective occupancies of 0.60299 and 0.39701. The H atom existed within hydrogen bonding of the SiO–H···NC_5H_5 part was refined to bond to the O atom rather than the N atom. A summary of cell parameters, data collection, and structure solution and refinements is given in Table S1.

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Keywords: phosphanylhydrosilylalkyne • group substitution effect • self-hydrosilylation • 1,1-carboboration • $B(C_6F_5)_3$

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Table of Contents

A Key Topic: Functionalized Alkyne

Text: Reactions of phosphanylhydrosilylalkynes with $B(C_6F_5)_3$ produce compounds of several types, which are results from differed reaction patterns induced due to the substituents effected on the C≡C bond.